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H. Ravner and P. J. Sniegoski
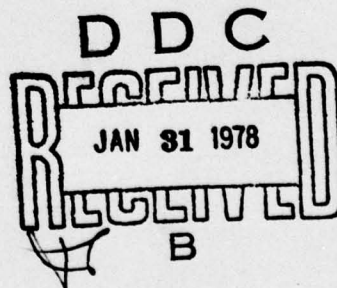
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The preliminary phase of a joint NRL/NAPTC study of additive depletion in an ester-based formulation has been concluded; a high-temperature deposition tester was employed as the test system under both aeration and nitrogen blanket conditions. An expression relating induction times and original concentrations of two amine inhibitors was devised based on simple kinetics of an inhibited system.

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ADDITIVE REACTIONS IN HIGH TEMPERATURE
DEPOSITION TESTS

INTRODUCTION

Navy aircraft gas turbine lubricants conforming to Specification
MIL-L-23699 encounter operating temperatures ranging from minus 40°C
at startup to 260°-290°C in the hottest engine areas. Bearing and main
shaft temperatures may rise even higher due to heat soak-back after
landing. One of the more serious problems arising from the heat burden
on the lubricant is the formation of deposits on shafts and bearings,
necessitating frequent overhauls and high maintenance costs. To help
predict the deposit-formation tendencies of these oils, the Naval Air
Propulsion Test Center (NAPTC), Trenton employs a device termed a "High
Temperature Deposition Tester" (HTDT) in which oil is recycled in a
prescribed routine past a gradient-heated tube; the type and quantity of
deposits formed on the tube surface and the amount of solids retained on
a line filter are all a measure of the stability of the oil with respect
to the formation of solids (1).

In the course of an on-going joint NRL-NAPTC study of lubricant-
additive chemical interactions at elevated temperatures in engine
environments it became apparent that HTDT runs would not only provide
deposition data, but could also yield qualitative chemical and kinetic
data on the role and fate of the oxidation inhibitors as well. A program
was therefore instituted in which NAPTC subjected a pentaerythritol
ester-base, antioxidant-containing fluid of the type used in MIL-L-23699
formulations to runs in the HTDT rig under a variety of operating
conditions; samples were periodically withdrawn for subsequent analysis
at NRL. The present report summarizes the results to date of this
study.

EXPERIMENTAL

The formulation employed in these experiments was a commercial
pentaerythritol ester of primarily pentanoic acid containing varying
proportions of the antioxidants phenyl-1-naphthylamine (PANA) and
dioctyl diphenylamine (DODPA). Initially, the additives were analyzed
by GLC using columns of 15 percent Dexsil-300 on Chromosorb W solid
support. It was found, however, that after oxidation in the HTDT
apparatus a degradation product of the ester was generated which over-
lapped the DODPA chromatographic peak and precluded analysis of the
latter component; a wide variety of column packings were examined but
they provided no improvement in the separation of the components. A

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thin layer chromatographic (TLC) method was therefore developed which
permitted analysis of the additives (2). Since the results using this
procedure provided much of the basis for the study, an outline of the
method is given here.

The equipment required for the TLC analysis included precoated 0.25
mm thick E. Merck Silica gel 60 F-254 10 x 20 cm plates, Centaur 100
microliter pipette with disposable plastic tips, Analtech 2-microliter
disposable micro-pipettes, Chromato-Vue Model CC-20 viewing cabinet.
Plates were precleaned by development in acetone and air dried one hour
before use. The samples were diluted 3 to 1 with heptane and applied as
duplicates in six 2-microliter spots along the 20 cm length of the plate
1.5 cm from the base. Standards containing 2, 1, 0.5, 0.3, 0.1, and
0.05 percent of each additive in the ester were prepared and spotted in
duplicate on the plates. The spotted plates were developed in 50-50-
heptane-toluene until the solvent front had risen 7.5 cm. Visualization
of the additives on the air-dried plates was carried out in two ways:

1) Visualization in short wave UV light. The additive spots
appeared as dark spots on the glowing green background of the plate.
The 0.05 percent concentrations were just visible.

2) Examination in white light. After 24 hours the additive spots
developed color and were conveniently viewed in white light. The 0.05
percent concentration was just visible. The R_f value (the ratio of the
distance the component rises above the origin to the distance the solvent
front rises) for DODPA is 0.76 and for PANA is 0.56. The base ester was
not visible under the shortwave UV but could be detected in white light
as a faint smudge with an R_f of about 0.1. Estimation of the additive
concentrations was carried out by a visual comparison to the standards,
with interpolation between values where necessary.

To provide information on deposit formation and additive depletion
under simulated engine conditions, HTDT runs were usually programmed
with oil-in temperature of 150°C and oil-out (maximum tube temperature)
of 330°C, although other temperature limits were used on occasion. In
the usual case, the test formulations were saturated during the runs
with dry air to determine the effect of the presence of oxygen; however,
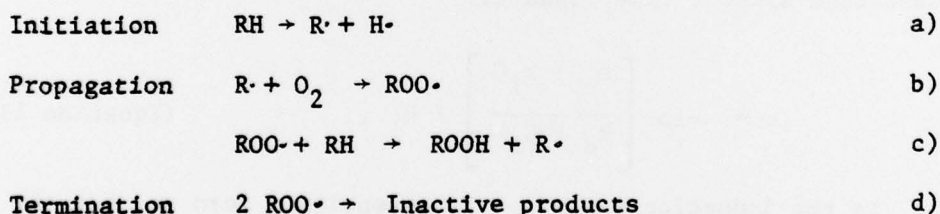in one series nitrogen was substituted for air.

The initial lubricant charge in the HTDT apparatus was approxi-
mately 250 ml. Runs were generally continued until the viscosity in-
crease of the oil approached 50 percent. There is some justification in
referring to the 50 percent viscosity point as the induction period
since a plot of viscosity vs time usually shows a sharp break in the
curve in this region. In early runs, losses due to sample withdrawals,
oil volatilization and degradation etc. were sufficiently large that
make-up fluid was required to continue the runs. Such additions obviously

affected additive levels and possibly influenced the additive-lubricant reactions because of the antioxidant replenishment; in any event, they made analytic treatment of the data highly uncertain. A series of runs was therefore conducted without the addition of make-up oil. The oil-in temperature was 150°C and the maximum tube temperature was 330°C. The experiments were terminated either at the end of the induction period, i.e., oil viscosity increased by 50 percent, or when fluid levels were so low, ca. 150 ml, that the system could not operate. Except where indicated this report will deal with the results of these latter series of experiments.
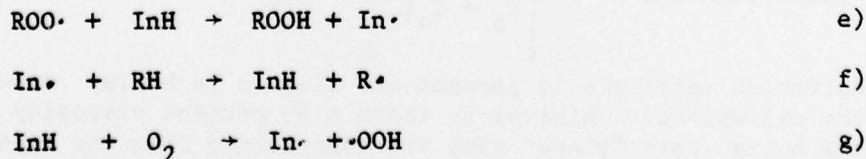
Analyses for additive contents were performed at NRL; viscosity and tube deposit measurements were made at NAPTC. The original NAPTC formulation used in each HTDT run is designated in the Tables by a PE-5L prefix; the runs themselves are identified by their NAPTC test numbers. In some instances, repeat runs with different test numbers were conducted to obtain different types of information, e.g., induction time, additive analysis, deposits, etc.

RESULTS AND DISCUSSION

Table 1 summarizes the results of the analyses for additive contents. With few exceptions, which are discussed in a later section, their concentrations decreased to only nominal amounts when the end of the induction period was reached. Before we discuss the factors affecting the kinetics of the additive depletion processes, it will be useful to review briefly the general mechanisms leading to the oxidation of the ester lubricant and the reactions of the additives. The air oxidation of hydrocarbons, esters, and many related organic compounds proceeds by an autocatalytic chain reaction:

$$\text{Initiation} \qquad RH \rightarrow R\cdot + H\cdot \qquad\qquad\qquad a)$$

$$\text{Propagation} \qquad R\cdot + O_2 \rightarrow ROO\cdot \qquad\qquad\qquad b)$$

$$ROO\cdot + RH \rightarrow ROOH + R\cdot \qquad\qquad c)$$

$$\text{Termination} \qquad 2\,ROO\cdot \rightarrow \text{Inactive products} \qquad d)$$

The overall reactions in an inhibited system can be generalized as follows:

$$ROO\cdot + InH \rightarrow ROOH + In\cdot \qquad\qquad e)$$

$$In\cdot + RH \rightarrow InH + R\cdot \qquad\qquad\qquad f)$$

$$InH + O_2 \rightarrow In\cdot + \cdot OOH \qquad\qquad\qquad g)$$

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Equation (c) represents the early stage of the autoxidation of the oil; it involves the abstraction of a hydrogen atom from a molecule of the oil by a peroxy radical to form a hydroperoxide, and an active free radical R· which in turn quickly reacts with oxygen in the air to form another peroxy radical. In equation (e) preferential reaction of the peroxy radical with an inhibitor tends to quench the reaction, provided the In· radical is relatively inactive. Therefore, for effective inhibition reaction (f) should be very slow compared to reaction (c). It is also expected that some of the inhibitor, especially at elevated temperatures, will also react directly with atmospheric oxygen, reaction (g). The significance of these reactions is to demonstrate that the inhibitor can be depleted by two routes, one by the reaction with peroxy radicals and the other by reaction with atmospheric oxygen. Obviously there are various secondary reactions here that could further complicate the situation; these will not be considered here.

Under operating conditions in the High Temperature Deposition Tester, it is assumed that ROO· radicals are generated at a constant rate, corresponding to a zero order reaction which does not depend upon the amount of additive present. Rate of depletion of the inhibitor by oxygen, on the other hand, depends upon the concentration of the additive and the concentration of oxygen. Since air is continuously passed through the oil, the concentration of oxygen is held constant and the reaction is therefore first order. The rate of additive depletion is thus postulated as:

$$\frac{-dC}{dt} = k_o + k_1 C$$

where C is the concentration of the inhibitor. Integration of this expression between C_o, the original concentration and C, the final concentration after t time leads to:

$$t = -\ln\left[\frac{k_o + k_1 C}{k_o + C_o k_1}\right] / k_1 . \qquad \text{(Equation 1)}$$

When t is the induction period, C is essentially zero so that the term $k_1 C$ drops out:

$$\text{induction time} = -\ln\left[\frac{k_o}{k_o + C_o k_1}\right] / k_1 \qquad \text{(Equation 2)}$$

Concentration terms are in percent and time is in hours. Since the time for the oil without inhibitor to reach a 50 percent viscosity increase was six hours, this "blank" time was substracted from the experimental values in the subsequent calculations. From the data in Table 2 best values were determined for the rate constants by substitution into equation 1. For PANA, $k_o = 0.0027$ percent hr^{-1} and $k_1 = 0.020$ hr^{-1}; for

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DODPA, k_o = 0.020 percent hr^{-1} and k_1 = 0.010 hr^{-1}. The k_o value for DODPA is six times that of PANA when expressed in the above units. When concentrations are expressed in moles per liter the k_o constant for DODPA is only three times as great. The two curves in Figure 1 were constructed from these values of k_o and k_1, substituted into Equation 2. Although only a small quantity of data were available, this somewhat simplified kinetic model reasonably fits the results.

If we consider a system in which there are two additives present that inhibit independently while both are undergoing oxidation, equation 2 can be used to predict the resulting induction time. Assume that either PANA or DODPA inhibits the system until the additive is completely depleted; time t for depletion to occur is calculated from equation 2. At the end of this time, the concentration of the other additive changes from C_o to $(C_o e^{-k_1 t})$ because of its oxidation in air; now the induction time of this additive at the new concentration can also be calculated. Similar calculations are also made based upon the assumption that the other additive reacts first. Predicted induction times can thus be given as a range of two values. In Table 3 the first value of the predicted range for the additive mixtures was determined as if DODPA inhibited initially. In each such case the expected range for the induction period is greater than that actually found. Application of Student's t-test in the 0.05 probability range shows a significant difference between experimental values and the mid-values of the predicted ranges. Thus some type of interaction between the two additives is suggested. Confirmation of this by TLC results is given in a later section.

The HTDT and analytical data indicate that in formulations containing mixtures of the two additives, PANA is depleted faster than DODPA, e.g. in Test Nos. 531 and 547 the ratio of DODPA to PANA became progressively larger as the testing proceeded. Such a trend is not entirely unexpected, and the ratio of the induction times of two additives of equal starting concentrations is commonly used as a rough way of evaluating the relative reaction rates of the inhibitors with the peroxy radicals. The inhibitor which reacts faster with these radicals will have the longer induction time since it is more effective in quenching the chain reaction and thus limits the generation of additional radicals. If the two additives were used together it would thus be reasonable to expect that the more effective additive would be preferentially consumed since it would react with more free radicals than the less efficient one.

Thin layer chromatograms of samples taken during the testing periods revealed components other than the two original additives. Components that fluoresce brilliantly under long wave UV light were readily seen in freshly developed TLC plates. After several hours the fluorescence diminished and was replaced by colors visible in white light. In systems that reached the end of the induction period, TLC revealed only brownish-orange materials that remained at the origin of

spotting. Although no attempt has yet been made to clarify these observations, it is speculated that the brightly colored components are derivatives of the additives as they are progressively oxidized. Chromatograms of samples of mixtures of the additives showed, during the early periods of testing, several components that did not form when the additives are used separately in the base oil. As mentioned earlier, this suggests interaction of the two additives.

The loss of the additives by oxidative degradation during the HTDT runs was confirmed in a different series of experiments. Formulation PE 5L-685, containing 1.0 percent each of PANA and DODPA, was subjected to four HTDT runs in which oil-in and oil-out temperatures ranged from 149°C to 204°C, and 330°C to 399°C respectively, Table 4. The calculated organic nitrogen content of this formulation due to the additives was 0.13 weight percent; the analyzed content (by a commercial laboratory) was 0.10 percent. In these runs, varying amounts of make-up PE 5L-685 were added as required. As seen in Table 4, in the course of these runs analyzed nitrogen contents remained essentially unchanged, even though the original additives had in some cases been completely depleted. (That the nitrogen content did not increase due to makeup oil additions is probably a result of venting losses and sampling withdrawals.) It is reasonable to assume that the residual nitrogen represents oxidized additive content, particularly when taken in conjunction with the TLC results.

The presence or absence of HTDT tube deposits is of overriding significance from an operational point of view. It is obvious from the results in Table 5 that under aeration conditions, the base stock ester does not generate deposits. PANA, however, in concentrations above ca. 0.2 percent, was a major cause of deposit formation; DODPA, on the other hand, had essentially no such effect. When PANA and DODPA were simultaneously present, DODPA did not inhibit the PANA-induced deposits. From the data in Table 5 where aeration conditions were used, a plot of the original percent PANA vs. the milligrams of deposit was constructed, as shown in Figure 2. The regression line calculated by the least squares method gives:

Mg tube deposits = (470) (% PANA) - 70

When the HTDT tests were conducted in an atmosphere of nitrogen, Table 5, no deposits were generated, even under very high oil-inlet and outlet temperatures. Although the scope of the present study did not include the chemistry of deposit formation, the interaction of PANA with oxygen to produce these deposits and the inertness of DODPA in this respect are of great practical interest and significance, and their causes should be pursued.

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SUMMARY AND CONCLUSIONS

The preliminary phase of a joint NRL/NAPTC study of additive deple-
tion in an ester-based formulation was concluded using the HTDT rig as a
test system. An expression relating induction times and original con-
centrations of PANA and DODPA inhibitors was devised based on simple
kinetics of an inhibited system. Predictions were generally satis-
factory where the inhibitors were used singly but less so with mixtures
of the two additives; interaction of the two additives is suspected.
PANA was shown to be a more effective inhibitor than DODPA; it was also
a more serious deposit generator under aeration, but not under a nitro-
gen blanket. From the data reported here, little advantage was seen in
the use of mixtures of the two additives either in extending the induc-
tion period or in reducing deposits under conditions in the HTDT rig.

FUTURE WORK

Based on the results of this preliminary study, a follow-on effort
will be continued as indicated:

1. Individual oxidation products of both PANA and DODPA will be
generated and identified to provide clues as to the separate roles they
play in the ester-inhibition process. This may be conveniently carried
out in controlled laboratory tests using the gas chromatograph-mass
spectrographic system now available in the Tribology Section.

2. A laboratory study will be made of PANA and DODPA (or other
model additive systems) to examine their interactions in an ester base
under oxidizing conditions.

3. It would be advantageous if the continuing research effort
with NAPTC would include small engine testing of model formulations. A
realistic comparison could then be made with "real life" oil-additive
behavior and these kinetic model studies.

ACKNOWLEDGEMENT

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2. "Quantitative TLC Analysis of Amine Antioxidants in High-Temperature Jet Engine Lubricants", Paul J. Sniegoski, NRL Memo Report 3490, April 1977; also published in the Journal of Chromatographic Science 15, August 1977, p. 328.

Table 1

HTDT Analytical Data
Oil-In 149°C, Oil-Out 330°C
Aerobic Conditions

Run	Test Hrs.	% Additive PANA	DODPA	Viscosity Increase % at 37.8°C
1A - No Additive Present				
PE-5L-682		0	0	
Test 458-1	10	0	0	95
1B - PANA Present				
PE-5L-765		0.2	0	
Test 535-1	5	0.05	0	0.9
-2	50	(b)	0	50
PE-5L-766		1.0	0	
Test 541-1	84	(a)	(a)	50
PE-5L-767		2.0	0	
Test 545-1	25	1.5	0	4.9
-2	50	0.1	0	11
-3	76	(b)	0	14
1C - DODPA Present				
PE-5L-768		0	0.2	
Test 540-1	8	0	(b)	21
-2	10	0	(b)	45
-3	12	0	(b)	96
PE-5L-769		0	1.0	
Test 678-1	50	0	(a)	25
PE-5L-770		0	2.0	
Test 673	79	0	(b)	65
1D - PANA and DODPA Present				
PE-5L-738		0.2	0.2	
Test 488-1	36	(a)	(a)	50
PE-5L-749		0.2	1.0	
Test 519-1	25	(b)	0.4	6.2
-3	37	(b)	0.1	7.8
-4	54	(b)	(b)	62
PE-5L-771		0.2	2.0	
Test 548-1	25	(b)	0.6	7.0
-3	37	(b)	0.07	23
-4	54	(b)	(b)	54
PE-5L-685		1.0	1.0	
Test 547-1	25	0.2	0.5	20
-2	50	0.1	0.3	31
-3	75	0.05	0.2	66
PE-5L-746		2.0	1.0	
Test 531-1	25	0.2	0.5	8.2
-3	65	(b)	0.1	
-5	80	(b)	0.05	37

(a) No analyses performed for additive content.

(b) Additive content below detectable limit of 0.05 percent.

Table 2

Effect of Individual Additive Concentration
on Induction Times

Test No.	Orig. % PANA	DODPA	Induction Time (Corrected)
545	2.0	0	134
541	1.0	0	84
535	0.2	0	44
540	0	0.2	7
678	0	1.0	49
673	0	2.0	71

Table 3

• Effect of Mixed Additives on Induction Times

Test No.	Orig. % PANA	DODPA	Induction Time (Corrected)	Calculated Range of Induction Time
488	0.2	0.2	30	43 – 45
531	2.0	1.0	79	132 – 140
548	0.2	2.0	79	82 – 91
547	1.0	1.0	63	104 – 137
519	0.2	1.0	49	62 – 68

Table 4

Organic Nitrogen Contents of HTDT-Subjected Oil

Sample	Test Hours	% PANA	DODPA	% Nitrogen Found
PE5L-685		1.0	1.0	0.10[a]
	Oil-In 149°C	Oil Out 330°C		
431	25	0.1	0.5	[b]
	50	0.1	0.5	.09
	75	0.05	0.3	.09
	110	0.1	0.1	.09
	Oil-In 149°C	Oil-Out 343°C		
425	50	[c]	0.2	[b]
	100	[c]	0.1	[b]
	110	[c]	0.05	0.12
	Oil-In 204°C	Oil-Out 385°C		
430	7	[c]	0.1	0.08
	10	[c]	[c]	
	12	[c]	[c]	0.10
	Oil-In 204°C	Oil-Out 399°C		
429	3	0.2	0.3	[b]
	4.5	[c]	[c]	[b]
	6	[c]	0.1	[b]
	7	[c]	[c]	0.10

(a) Calculated organic nitrogen content based on original additive content is 0.13 weight percent.

(b) No analyses performed for additive content.

(c) Additive content below detectable limit of 0.05 percent.

Table 5

Tube Deposits

Air Atmosphere
Oil-In 149°C   Oil-Out 330°C

Test No.	Tube Deposits, mg.	Original % PANA	DODPA
458	2	0	0
545	978	2.0	0
531	712	2.0	1.0
547	480	1.0	1.0
541	419	1.0	0
535	13	0.2	0
540	8	0	0.2
673	0	0	2.0
519	3	0.2	1.0
548	2	0.2	2.0

Nitrogen Gas Atmosphere
Oil-In 149°C   Oil-Out 330°C

473	1	1.0	1.0

Oil-In 204°C   Oil-Out 413°C

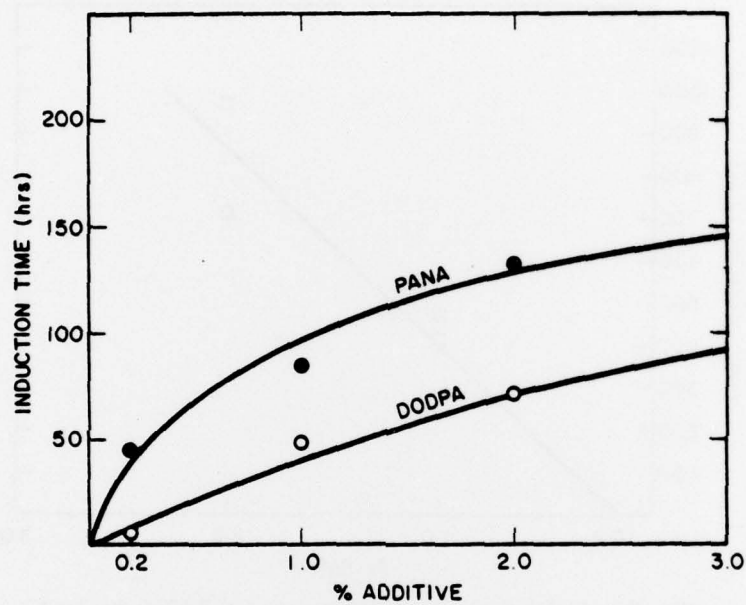|			
474	1	1.0	1.0

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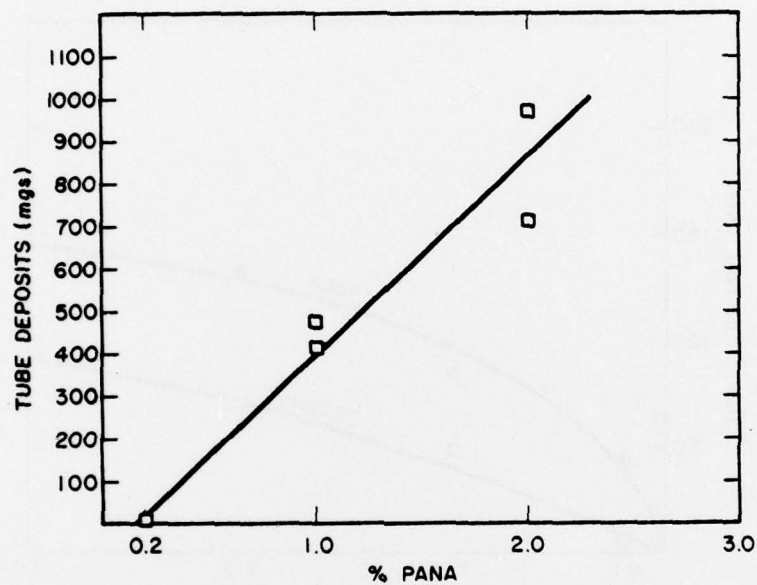
Fig. 1 — Induction time as a function of additive content

Fig. 2 — Tube deposits as a function of PANA content